

## Positronium Characterization of Nanopores in Technologically Modified MgO-Al<sub>2</sub>O<sub>3</sub> Ceramics

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It is established that positron annihilation lifetime spectroscopy can be successfully used as a porosimetry method to study of nanopores size and transformation of free volume in humidity-sensitive MgO-Al<sub>2</sub>O<sub>3</sub> ceramics in adsorption-desorption cycles using lifetimes of ortho-positronium-related components. It is shown that the fourth component gives information about water-free volume or nanopores size, while the third component reflects positronium trapping both in nanopores and in water “bubbles”.

**Keywords:** Spinel, Ceramics, Positronium, Nanopores, Water-immersion, Drying.

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### 1. INTRODUCTION

It is known that the ceramics with spinel structure are one of the best porous materials for humidity sensors [1]. Functional MgO-Al<sub>2</sub>O<sub>3</sub> ceramics are thermally and chemically stable in comparison with other types of porous materials with a short time to changes in humidity operation.

As was shown early [2,3], the functionality of humidity-sensitive spinel ceramics is dependent on microstructure of grains, grain boundaries and pores. These elements significantly affect on their nanostructurization. In addition, electrical properties of ceramics depend on the sorption processes in these materials.

Traditionally, microstructural characteristics of ceramic materials are studied using X-ray diffraction, electron microscopy, porosimetry methods, etc. However, the methods of mercury and nitrogen porosimetry provide information on open pore with radius  $> 5$  and  $> 2$  nm, respectively [4]. Physical processes in ceramics depend not only on the number and nature of large open pores, but also on the closed nanopores [5]. So for more information on these structural components and their influence on the properties of MgO-Al<sub>2</sub>O<sub>3</sub> ceramics, reasonable to use additional methods of structural characterization, which would allow to study the closed and open pores and other free-volume entities on the nanoscale level. In this case we used positron annihilation lifetime spectroscopy (PALS) tools to study free-volume transformation in spinel ceramics caused by different sintering temperature as porosimetry methods [3]. In this work we would like to study sorption ability of MgO-Al<sub>2</sub>O<sub>3</sub> ceramics sintered at 1100 °C in different stage of water-immersion and drying.

### 2. EXPERIMENTAL

The MgO-Al<sub>2</sub>O<sub>3</sub> ceramics were sintered at 1100 °C for 2 hours using traditional ceramic technology [2,3,5-8]. The PALS investigation were performed using ORTEC

spectrometer (<sup>22</sup>Na source) [6]. High-statistical investigations were held in several stages after following procedures further processing samples. The initial measurements were performed on ceramic samples dried in vacuum at 120 °C for 4 hours. To study the interaction of connectivity porous ceramic structures, the same samples were moistened by water (placed in a distiller, the relative humidity was 100 %) for 8 hours (1 day) at 22 °C. PALS measurements were repeated at 1, 2, 3 and 7 days after the procedure. At the last stage samples of MgO-Al<sub>2</sub>O<sub>3</sub> ceramic were dried again in a vacuum at 120 °C for 4 hours and repeated measurement to determine of PALS reversibility of physical adsorption of water molecules at exactly the same temperature. To maximum assessment of free volume in ceramics and calculation of nanopores size, the PALS spectra were decomposed by LT computer program into four components with positron lifetimes  $\tau_1$ ,  $\tau_2$ ,  $\tau_3$  and  $\tau_4$  and intensities  $I_1$ ,  $I_2$ ,  $I_3$  and  $I_4$ . The errors were  $\pm 0,005$  for  $I_3$  and  $\pm 0,0001$  for  $I_4$ .

### 3. RESULTS AND DISCUSSION

As we shown early [5-8], in the case of humidity-sensitive MgO-Al<sub>2</sub>O<sub>3</sub> ceramic, there are two channel of positron annihilation: positron trapping ( $\tau_1$  and  $\tau_2$  lifetimes) and ortho-positronium o-Ps decaying within “pick-off” annihilation ( $\tau_3$  and  $\tau_4$  lifetimes). The first component is reflect microstructural species of spinel, the second one correspond to positron trapping defects located near grain boundaries. The third and fourth components are due to “pick-off” annihilation of o-Ps in nanopores filled by water.

As expected, the parameters of the first component ( $\tau_1$ ,  $I_1$ ) practically unchanged since sorption processes do not affect on the structural features of spinels (Table 1). The lifetime of second defect-related component  $\tau_2$  is near  $\sim 0.46 \pm 0.48$  ns and the intensity  $I_2$  is  $\sim 0.28$ . As a result, the positron trapping parameters calculated within two-

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**Table 1.** Fitting parameters for MgO-Al<sub>2</sub>O<sub>3</sub> ceramics mathematically treatment with four-component fitting procedure

Pre-history	$\tau_1$ , ns	$I_1$ , a.u.	$\tau_2$ , ns	$I_2$ , a.u.	$\tau_3$ , ns	$I_3$ , a.u.	$\tau_4$ , ns	$I_4$ , a.u.
After drying	0.169	0.68	0.462	0.28	2.240	0.017	70.11	0.025
1 days	0.170	0.66	0.483	0.28	1.820	0.044	53.05	0.009
2 days	0.170	0.65	0.457	0.29	1.762	0.043	55.26	0.011
3 days	0.171	0.67	0.484	0.28	1.784	0.040	59.64	0.011
7 days	0.167	0.67	0.462	0.29	2.145	0.026	62.74	0.013
After drying	0.172	0.68	0.459	0.29	2.215	0.021	68.29	0.019

**Table 2.** Positron trapping modes and transformation of free volumes in MgO-Al<sub>2</sub>O<sub>3</sub> ceramics sintered at 1100 °C after different duration of drying

Pre-history	$\tau_{av}$ , ns	$\tau_b$ , ns	$\kappa_d$ , ns <sup>-1</sup>	$R_3$ , Å	$\sim f_{v3}$ , %	$R_4$ , Å	$\sim f_{v4}$ , %
After drying	0.254	0.21	1.10	3.09	0.38	18.44	11.75
1 days	0.263	0.21	1.15	2.71	0.66	15.39	2.43
2 days	0.258	0.21	1.14	2.65	0.61	15.77	3.30
3 days	0.264	0.21	1.13	2.67	0.57	16.54	3.78
7 days	0.257	0.21	1.16	3.01	0.55	17.08	5.02
After drying	0.257	0.21	1.08	3.07	0.46	18.10	8.36

state positron trapping model [6], such as average positron lifetime  $\tau_{av}$  and positron lifetime in defect-free bulk  $\tau_b$  unchanged, while positron trapping rate of defect  $\kappa_d$  slightly increases after water-immersion (Table 2). Major changes caused by sorption of water observed in the third and fourth o-Ps-related components. It is established that the number of nanopores correspond to the intensity of third and fourth components [3, 5]. Thus, the intensity  $I_4$ , which corresponds to the number of larger nanopore radius  $\sim 18$  Å, significantly decreases after 1 day after water-immersion. The lifetime  $\tau_4$  decreases which reflects lessening of nanopore radius calculated within Tao-Eldrup model (Table 1). It is connected with penetration of nanopores by water molecules (fully or partially filling) changing characteristics of o-Ps-related component. Obviously, such pores should have access to environmental and internal communications at the nanoscale.

As the intensity  $I_4$  does not fall to zero and is near 0.9%, it should be assumed that part of the nanopore where the disintegration of o-Ps atoms, is closed. Closed pores in ceramics can also be seen in micrograph [3,8]. Obviously, the grains growth and the formation of closed porosity begins at the nanoscale. PALS method also provides information on the phase separation in the early stages, which contributes to a closed porosity.

Additional studies of MgO-Al<sub>2</sub>O<sub>3</sub> ceramics after 2, 3 and 7 days after water-immersion shows a gradual increase in the lifetime  $\tau_4$  and intensity  $I_4$ , indicating release of water from the inner voids of ceramics.

After final drying in vacuum at 120 °C for 4 hours, the initial distribution of pores in MgO-Al<sub>2</sub>O<sub>3</sub> ceramics tends to recovery. However, the parameters of the fourth component is not fully recovered, testified that some water molecules remaining adsorbed.

Transformation of free volume caused by moisture sorption processes in ceramics MgO-Al<sub>2</sub>O<sub>3</sub>, sintered at 1100 °C, given also in Table 2. Besides nanopore with radius  $R_3$  and  $R_4$  calculated by the model Tao-Eldrupa, defined contribution corresponding to free volume (nanopores) by semi-empirical equation [9]:

$$f_v = C \cdot V_f \cdot I_{o-Ps}, \quad (1)$$

where  $V_f = 4/3 \cdot \pi \cdot R_{o-Ps}$  – free volume calculated from lifetimes of o-Ps-related components;  $I_{o-Ps}$  – intensities of o-Ps-related components, C – empirical parameters (0,0018).

The most significant changes caused by moisture sorption processes are observed for the largest nanopore radius of  $\sim 18$  Å. The intensity of this component does not return to initial value after drying of ceramics, because not all water released into the nanopore interior. Reducing the value of the lifetime  $\tau_4$  after drying of ceramics with poorly developed porosity can be due to the formation of thin layers of water molecules surrounding the large pores that completely freed moisture at 120 °C.

The lifetime  $\tau_3$  decreases after water-immersion of ceramics with a gradual increase in drying and intensity  $I_3$  grows, indicating annihilation of o-Ps in water-filled nanopores (Table 1). The presence of water in the nanopores of smaller radius  $\sim 3$  Å after drying reflects in increasing of intensity  $I_3$  and a slight decreasing of lifetime  $\tau_3$ . It is noted that the lifetime of o-Ps  $\sim 1,8$  nm reflects the annihilation in the water "bubbles" with radius near 3 Å. Its number increasing in accordance with intensity  $I_3$ .

#### 4. CONCLUSION

It is shown that lifetimes of third and fourth o-Ps-related component of PALS spectra decreases in water-immersed MgO-Al<sub>2</sub>O<sub>3</sub> ceramics reflected decreasing of free-volume after water-immersion. The amount of biggest nanopores decreases, while positronium trapping in smaller nanopores carried out simultaneously with annihilation in water "bubbles".

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